

RECENT DEVELOPMENTS IN CHROMATOGRAPHIC EXTRACTION
BY MEANS OF SYNTHETIC POLYMERS AND THEIR APPLICATION
TO INORGANIC ANALYSIS

C. Pointre naud

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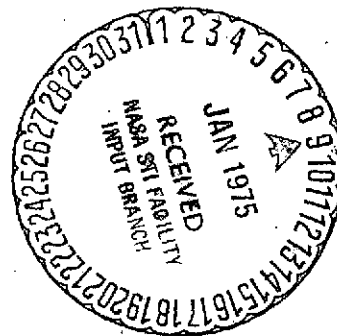
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16. Abstract The application of chromatographic methods to extraction by solvents calls for the choice of carriers able to retain firmly one of the two aqueous or organic phases. For this purpose synthetic polymers may be used which have high mechanical and chemical resistance and which may be obtained in a porous state. An aqueous phase may be quite firmly retained by an ion exchange resin possessing water absorbent groups. As against this, organic solvents may be fixed on inert polymers such as tetrafluoropolyethylene. The equilibria involved may differ greatly depending on the nature of the extracted species. Various possible cases are described and illustrated by examples.			
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RECENT DEVELOPMENTS IN CHROMATOGRAPHIC EXTRACTION
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Introduction

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Although modern methods of measurement are frequently extremely sensitive, they are not selective enough to make it possible to measure any element in a mixture directly. Frequently the element must be separated from several other obstructive elements so that measurement can be performed.

One of the most important methods of separation is extraction by solvents, which involves the partition of compounds into two immiscible liquid phases. The constant of partition of a compound into two solvents is appreciably equal to the ratio of the solubilities of this compound in each of the two solvents. Thus the two compounds may be separated by varying the differences in solubility between them.

However, the possibilities offered by extraction methods are considerably increased by the fact that it is possible to vary the apparent solubility of a compound. For example, a substance /40 may be kept in aqueous phase by making it participate in chemical reactions in this phase (acid-base or oxidation-reduction reactions or the formation of complexes). On the other hand, it is possible to encourage the extraction of a compound by increasing its solubility in the organic phase by the addition of a complexing agent.

By manipulating all the factors available (choice of pH and

*Numbers in the margin indicate pagination in the foreign text.

reactants in aqueous solution, choice of complexing agent in organic solution), it is frequently possible to determine conditions in which a few successive extractions are all that is necessary for quantitative separation of two given compounds. In some cases, however, especially in attempts to separate elements with similar chemical properties, separation may require a large number of successive extractions or the use of a continuous extraction device in which there is a countercurrent flow of the two aqueous and organic phases. No matter what solution is chosen, separation can be performed only by means of a cumbersome setup which is difficult to use in the laboratory.

It is for this reason that a number of investigators have attempted to apply chromatographic techniques to extraction. With the use of simple equipment, chromatography makes it possible to obtain a large number of equilibria between two phases in a column.

The first attempts followed the discovery of partition chromatography by Martin and Synge in 1941. The first separations performed primarily involved organic mixtures. The carriers used were silica gel, porous diatomites, starch, cellulose, rubber, etc. Many precautions were necessary in preparing columns from these substances so that adsorption phenomena would not be added to the partition phenomenon, since adsorption results in spreading of the elution peaks and decreases the efficiency of the columns.

Development of the application of partition chromatography to inorganic analysis using the same carriers has been quite limited. The most important current problem in this area is the separation of mineral ion species with a low solubility in organic solvents; this is frequently solved by means of ion exchangers.

Still more recently, two findings have indicated the possibility of significant applications of partition chromatography to inorganic analysis. First, there was the production of porous or finely divided synthetic polymers such as polystyrene, polyethylene, fluorine derivatives of polyethylene, and polyvinylchloracetate, with high mechanical strength and chemical resistance. Second, there was the extension of extraction by solvent, due primarily to the determination of the extractive properties of a number of organic substances such as β -diketones, alkylphosphoric acids, and long-chain amines.

These new methods of separation usually appeared as applications of chromatographic techniques tending to improve and facilitate already known separations which could be performed by extraction, and it is for this reason that they may be considered under the term "chromatographic extraction."

From a technical standpoint, the problem is to find a finely divided carrier which firmly retains one of the two phases, aqueous or organic. The following discussion will make use of examples to present various ways of solving this problem by means of synthetic polymers.

Chromatographic Extraction

Aqueous Phase as Stationary Phase

One especially attractive way of immobilizing an aqueous phase is to use an ion exchange resin as a carrier. Resins are extremely water-absorbent and fix the aqueous phase very firmly, thus making it equivalent to a highly concentrated ionic solution; the electrolyte cannot be removed by mere washing since it is integral to the matrix of the resin. In addition, ion exchange resins, which are plastics with high strength and mechanical resistance, occur in the finely divided state.

When the water-saturated resin is brought into contact with an organic solvent which is not miscible with water, it may be assumed that three phases are present: the resin grain, the organic solvent and, between the two, a film of water caused by the solvation of the functional groups present at the surface of the resin grain, among other factors.

This film of water may result in some disadvantages: specifically, it may provoke agglomeration of the grains into nodules (the grains being joined to each other by the water film). These nodules may be diminished by drying the resin slightly before it is brought into contact with the solvent, thus obtaining a uniform suspension of the grains in the organic phase.

Two types of equilibria between the various phases present may occur:

- equilibria of partition between the organic phase and the aqueous film;
- equilibria of ion exchange and partition of molecules between the aqueous film and the resin.

Two situations may arise, depending on the nature of the species to be extracted in the organic phase.

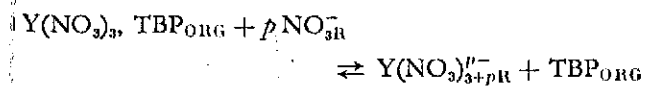
Extraction of Ion Association or Simple Covalence Compounds. Anion Exchange Resin

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For example, let us consider the case of yttrium nitrate, which may be extracted in toluene by means of an organic complexing agent: tributylphosphate or TBP. The form of the compound extracted in toluene is $Y(NO_3)_3 \cdot TBP$.

Extraction takes place in a nitrate medium. This case, therefore, calls for the use of an anion exchange resin in ionic nitrate form. Equilibria of the following type may occur between

the organic solution and the water-saturated resin:



if one assumes that yttrium can occur in the resin only in the form of neutral nitrate ($p = 0$) or anionic complexes ($p > 0$). The overall partition coefficient of yttrium, that is, the ratio of the total concentrations Y_R and Y_{ORG} of yttrium in each phase, is:

$$P = \frac{Y_R}{Y_{ORG}} = \frac{\sum K_p [NO_{3R}^-]^p}{[TBP_{ORG}]}$$

When the yttrium concentration in the resin is far from the saturation point, $[NO_{3R}^-]$ is a constant; this is the exchange capacity of the resin, and P basically depends on the TBP concentration in the organic phase.

The partition of yttrium between a Dowex I $[NO_3^-]$ resin and an 80% solution of TBP in toluene has been studied experimentally by Small [1] (Fig. 1). It may be seen that the partition coefficient of yttrium is low under these conditions. In addition, these experiments have shown the kinetics of the exchanger to be fairly slow, and as a result, the results afforded by chromatography are disappointing here. The slowness of the equilibria results in a spread of the elution peaks, as for example in the case of elution of a mixture of thorium nitrates and rare earths [1] (Fig. 2). The thorium is eluted by a solution of 50% TBP in xylene, and the rare earths are subsequently eluted more rapidly by increasing the TBP concentration of the eluant; as Fig. 2 shows, separation is not complete. An attempt was also made to separate rare earths, but it was possible only to separate the light rare earths from the heavy rare earths [1]. Very little work has been done on this subject so far.

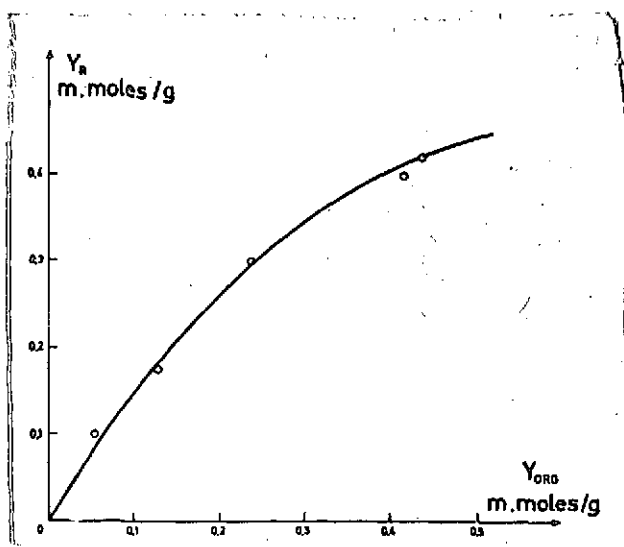


Fig. 1. Partition of yttrium between a Dowex-1-X4 resin (NO_3)(H_2O) and an 80% tributylphosphate solution in toluene [1].

It may be possible to improve the exchange kinetics by manipulating factors such as the temperature and granulometry of the resin. This might allow the possibility of other separations, such as that of halogenide or thiocyanate complexes, which may be fixed by anion exchange resins and extracted by solvents such as hexone.

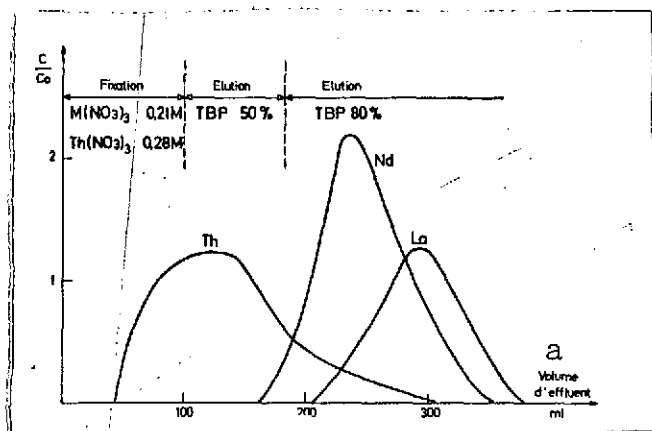


Fig. 2. Separation of thorium nitrates and rare earths by means of a column of Dowex-1-X4 (NO_3)(H_2O) and solutions of tributylphosphate in xylene [1].

Key: a. Quantity of effluent in ml

Extraction of Chelates. Cation Exchange Resin

Generally, a chelating agent is an organic compound with a mobile hydrogen which can be replaced by a metal to yield a highly stable cyclic complex which is soluble in solvents with low polarity.

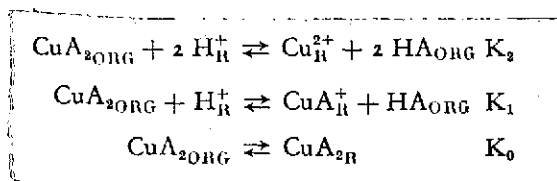
The partition equilibrium is thus an exchange equilibrium of two cations: the metallic cation and the proton. The aqueous phase should be able to furnish the protons, and thus a cation exchange resin in acid form will be used as a carrier for the aqueous phase in this case.

There are two possible situations, depending on whether the chelating agent has very low basic properties (the case with acetylacetone, for example) or whether it has very marked basic properties and is able to react with the protons of the resin (the case with oxine). /42

1) Chelating Agent with Low Basic Properties

Let us consider the example of acetylacetone $\text{CH}_3\text{-CO-CH}_2\text{-CO-CH}_3$, which will be represented here as HA.

Acetylacetone may be partitioned between the organic phase and the water-saturated acid resin, but it occurs in the resin only in the molecular form HA. If the organic solution contains copper(II)acetylacetonate, CuA_2 , the following equilibrium may occur:



The overall partition coefficient of copper is thus:

$$P = K_0 + K_1 \frac{[\text{H}_\text{R}^+]}{[\text{HA}_\text{ORG}]} + K_2 \frac{[\text{H}_\text{R}^+]^2}{[\text{HA}_\text{ORG}^2]}$$

When the resin is far from being saturated with copper, $[\text{H}_\text{R}^+]$ is close to the exchange capacity of the resin and the partition coefficient basically depends on the concentration of acetylacetone in the organic phase. Under these conditions, the theoretical curve $\log p = f[\log(\text{HA}_\text{ORG})]$ appears as shown in Fig. 3. The gradients -2, -1 and 0 indicate the presence in the resin of the species Cu^{2+} , CuA^+ or CuA_2 .

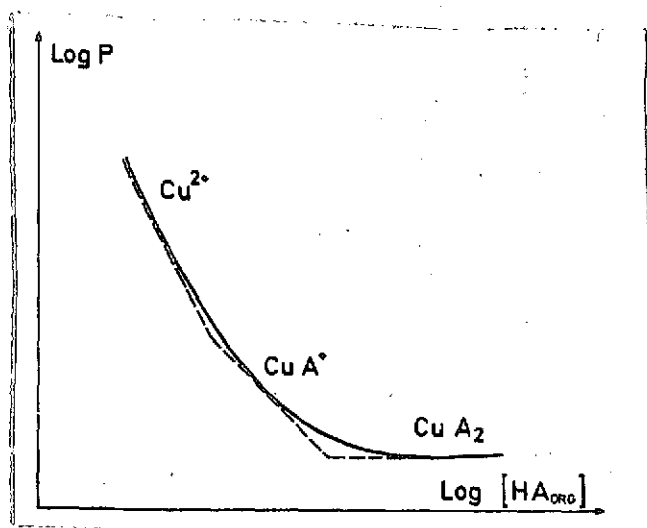


Fig. 3. Theoretical curve of variations in partition coefficient of copper (II) acetylacetonate on a water-saturated strong-acid resin as a function of the concentration of acetylacetone in the organic phase.

Curves of this sort have been determined experimentally [2] (Fig. 4) in the case of copper (II) and iron (III) with the highly acidic resin Dowex 50X2. The solvent used was benzene. The gradient -2 obtained for copper (II) indicates that Cu^{2+} predominates in the resin in the entire range of acetylacetone concentration examined. In the case of iron (III) there is a change from the gradient of close to -3 to a gradient

of -2, followed by a gradient of close to -1 when the acetylacetone concentration increases in the benzene phase. This indicates the presence of Fe^{3+} , FeA^{++} and FeA_2^+ in the resin, depending on the solution conditions, with FeA^{++} predominant, however.

The partition coefficients of acetylacetonates on a strong-acid resin are always quite high, since the resin is equivalent to a highly acidic aqueous phase, and the difficulty of extracting chelates by means of organic solvents is known to increase with the acidity of the aqueous phase. In an acid medium, the metallic element shows a preference for the aqueous phase, which is manifested by a high partition coefficient in the present case. /43

Thus it may be predicted that just as the extraction efficiency depends on the pH of the aqueous phase, the partition coefficient should depend on the acidity of the functional group of the resin. Figure 5 shows the variations of the partition coefficient curve of copper acetylacetonate on sulfonic, phosphonic and carboxylic resins.

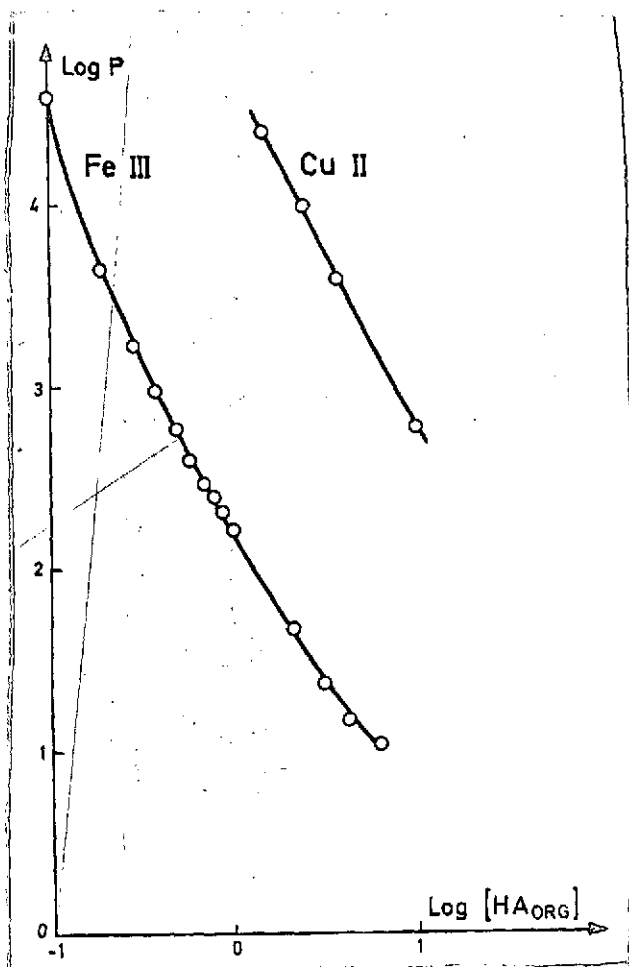


Fig. 4. Experimental curves of variations in the partition coefficient of copper (II) acetylacetonate and iron (III) acetylacetonate on Dowex-50-X2 sulfonic resin as a function of the concentration of acetylacetone in benzene [2].

The partition coefficient actually decreases as the acidity of the functional group decreases. The copper is fixed on sulfonic and phosphonic resin in the form of Cu^{2+} ions. In the carboxylic resin one finds both Cu^{2+} and CuA^+ ions (or rather the complexes, R_2Cu and RCuA , of these ions with the carboxylate groups).

Experiments show that the equilibria between cation exchange resins and acetylacetonates are not particularly slow. With a column one obtains theoretical plate heights of a few millimeters with strong-acid resins and on the order of a centimeter with weak-acid resins. The kinetics may undoubtedly be improved by working in temperatures

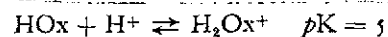
higher than the ordinary temperature. The following examples of separation by chromatographic extraction of chelates may be given:

- the frontal analysis of rare earths performed on sulfonic resin by Small, with diethylhexylphosphoric acid in solution in toluene as a chelating agent [1] (Fig. 6);
- the separation of uranyl acetylacetonate and copper (II) acetylacetonate on carboxylic resin [2] (Fig. 7).

2) Chelating Agent with Marked Basic Properties /44

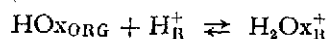
Let us consider the case of 8-hydroxyquinoline or oxine, which will be represented by HOx.

Oxine may react with the proton in an aqueous medium as follows:



Thus oxine can occur in a strong-acid resin only in the form H_2Ox^+ , the concentration of the HOx molecule, with low water-solubility, being negligible. Experiments show that oxine has an extremely high affinity for sulfonic acid resins. An acid resin saturated with water and placed in

contact with a benzene oxine solution fixes the oxine quantitatively according to the following reaction:



If a resin of this sort, saturated with H_2Ox^+ ions, is placed in contact with an aluminum oxinate AlOx_3 solution, aluminum fixation may be observed. The possible equilibria between the resin and the the organic solution are:

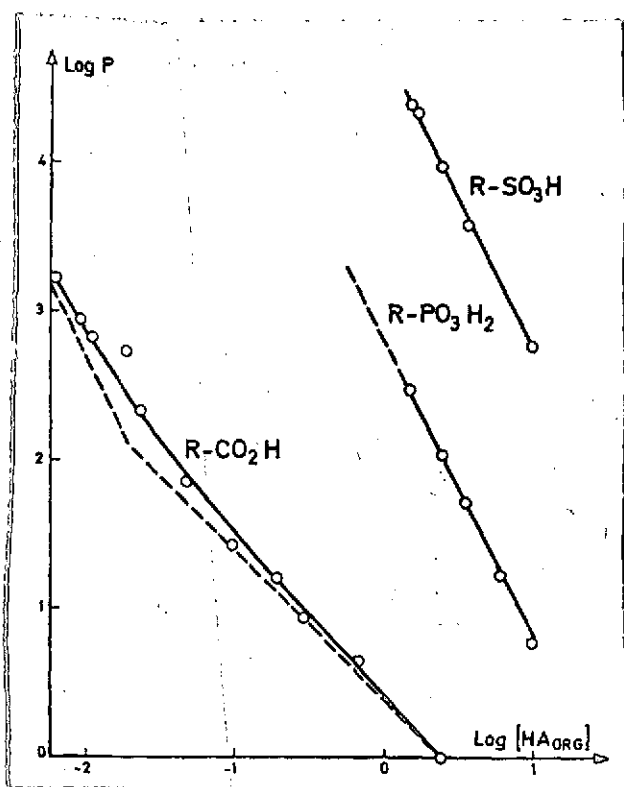


Fig. 5. Experimental curves of variations in the partition coefficient of copper (II) acetylacetonate on Dowex-50-X2 sulfonic resin, phosphonic resin (BioRex63) and carboxylic resin (IRC50) as a function of the concentration of acetylacetone in benzene [2].

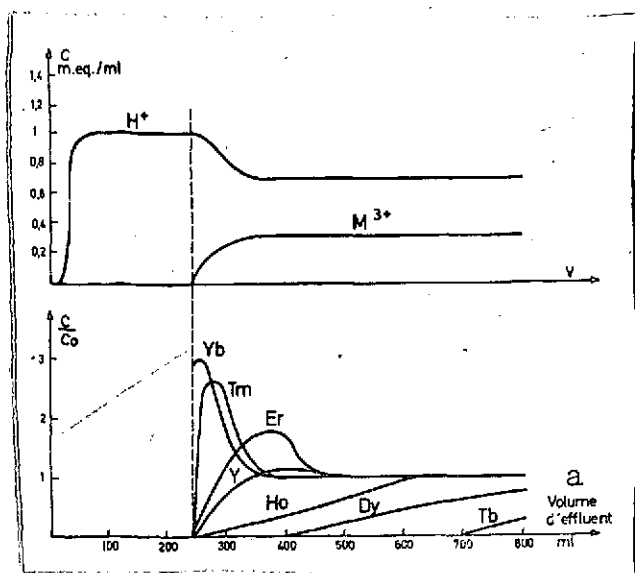


Fig. 6. Frontal analysis of a mixture of rare earths on Dowex-50-X4 resin (H^+)(H_2O) by means of 0.67 M diethylhexylphosphoric acid solution in toluene [1].

Key: a. Quantity of effluent in ml

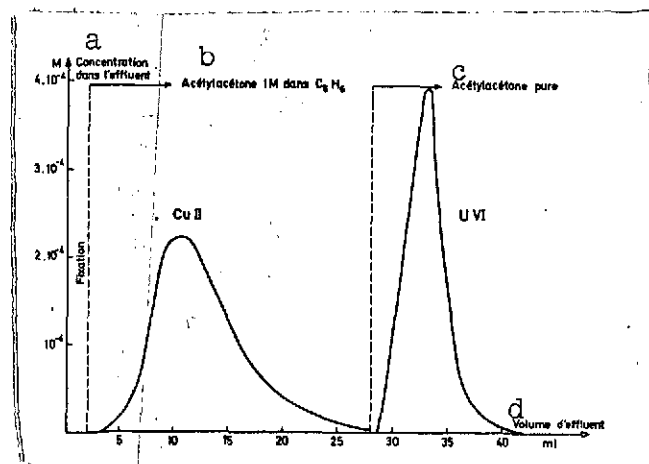
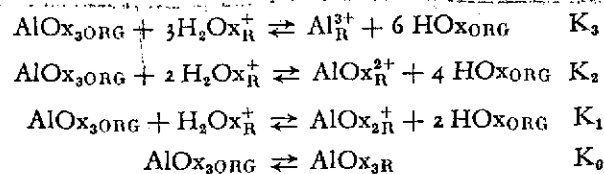


Fig. 7. Separation of copper (II) acetylacetonate and uranium (VI) acetylacetonate by means of a column of IRC50 carboxylic resin (RH , H_2O) and solutions of acetylacetone in benzene [2].

Key: a. Concentration in effluent
b. 1 M acetylacetone in C_6H_6
c. Pure acetylacetone
d. Quantity of effluent in ml



The overall partition coefficient of the aluminum is:

$$P = K_0 + \sum_{n=1}^{n=3} K_n \frac{[H_2Ox_R^+]^n}{[HOx_{ORG}]^{2n}}$$

When the aluminum content of the resin is far from the saturation point, $[H_2Ox_R^+]$ is equal to the exchange capacity and P basically varies with the oxine concentration in the organic phase to the $2n^{th}$ power (as opposed to the n^{th} power for acetylacetone).

Variations of P with the concentration of the complexing agent are much more rapid since the complexing agent has basic properties, while it does not.

Experiments yield a curve $\log P = f \log [HOx_{ORG}]$

with a gradient of -4, indicating that it is AlOx^{++} which is fixed in the resin within the range studied [2] (Fig. 8).

The exchange kinetics are very slow, however, since they are limited by the diffusion of large H_2Ox^+ and AlOx^{++} ions in the resin. So far, even the use of extremely porous resins has not permitted a sufficient improvement in the kinetics to allow for operation in a column.

The Organic Phase as the Stationary Phase

This is the case in which synthetic polymers are most attractive, since, in contrast to ion exchange resins, they show little affinity for water and retain organic solvents quite well.

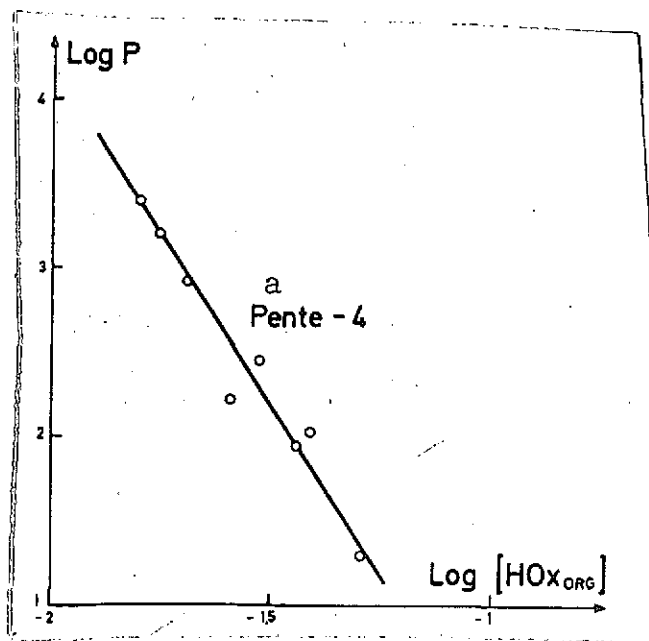


Fig. 8. Partition of aluminum oxinate between a Dowex-50-X4 resin (H^+ , H_2O) and a solution of oxine in benzene [2].

Key: a. Gradient: -4

The most frequently used polymers are:

- polytetrafluoroethylene (teflon) and polytrifluorochloroethylene (Kel-F) which are completely inert and may be obtained in a porous state;
- polyethylene;
- polystyrene (copolymer of styrene and divinylbenzene);
- polyvinylchloride.

Another very widely used carrier should be added to this list of polymers: cellulose powder.

This is a polar compound which easily retains water but which may also serve as a carrier for solid compounds such as amine chlorhydrates or organic solvents after treatment with water-repellent products. Cellulose is not completely inert, however; it manifests troublesome adsorptive properties for some cations and it is sensitive to concentrated acids.

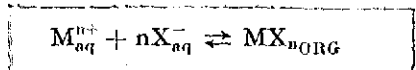
The properties of these carriers are not the same with regard to all solvents. For example, polar solvents are firmly fixed on teflon and Kel-F, while apolar solvents are most firmly fixed on polystyrene. Of the solvents studied, cyclohexanol and cyclohexanone appear to be the most firmly fixed on porous teflon, while benzene and chloroform are most firmly fixed on polystyrene.

The equilibria occurring between the polymer and the aqueous solution are solely partition or exchange equilibria between the two phases present. When the organic solvent (or the organic reactant dissolved in the stationary phase) is partially miscible with water, the mobile aqueous phase must be saturated with organic solvent (or reactant) before entering the column to preclude any carryover of the stationary phase, which would decrease the capacity of the column. /45

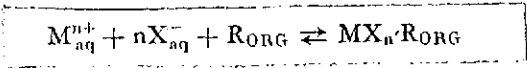
We will consider two more cases, depending on the nature of the species extracted by means of the stationary organic phase.

Extraction of Ion Association or Simple Covalence Compounds

In this case, the extraction equilibrium of a M^{n+} cation is generally in the simple form:



or, if extraction is encouraged by an organic reactant R:



The partition coefficient of element M thus depends on the X^- ion concentration in the aqueous phase and possibly on the concentration of the reactant R in the stationary phase. With a given column (that is, one with a stationary phase of given composition), selective elution may be obtained only by varying the concentration of the X^- ion in the eluant aqueous phase. This may be illustrated by two examples.

1) Extraction of Thiocyanates by Methyl Isobutyl Ketone (Hexone)

In this case the stationary phase is a pure solvent. In the presence of ammonium thiocyanate in an aqueous solution, zirconium occurs in the form Zr^{4+} , $Zr(SCN)^{3+}$, $Zr(SCN)_2^{2+}$, $Zr(SCN)_3^+$, ...; it may be extracted by hexone in the form $Zr(SCN)_4$. The overall partition coefficient of zirconium depends on the thiocyanate ion concentration. Experiments show this to be low in a 4 M NH_4SCN medium. The partition coefficient of hafnium in the same medium, however, is quite high. This fact enabled Fritz and Frazee [3] to perform zirconium-hafnium separation by means of a porous teflon column saturated with methyl isobutyl ketone (Fig. 9). Fixation of the mixture and elution of the zirconium occurred in the presence of 4 M ammonium thiocyanate. The hafnium remained fixed on the column and was eluted rapidly only when there was no thiocyanate in the eluant.

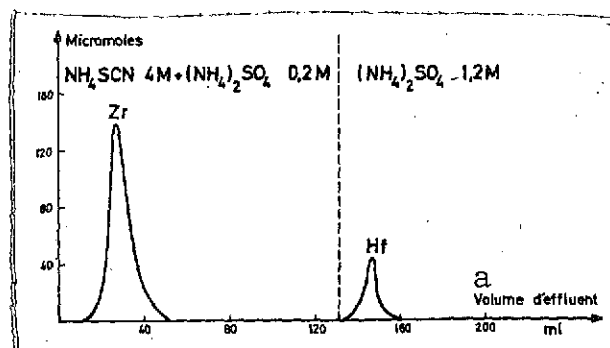


Fig. 9. Separation of zirconium and hafnium by means of a teflon column saturated with hexone and an aqueous solution of thiocyanate and ammonium sulfate [3].

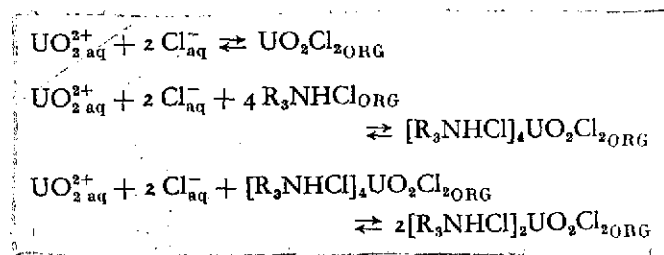
Key: a. Quantity of effluent in ml

2) Extraction of Chlorides by Trilaurylamine in Solution in Cyclohexanol

The partition of uranyl chloride between an aqueous hydrochloric acid solution and a 0.8 M trilaurylamine solution in cyclohexanol fixed on a porous Kel-F carrier has

been studied by Petit-Bromet [4].

Uranium may be extracted by means of an organic solution in three forms: UO_2Cl_2 , $\text{UO}_2\text{Cl}_2(\text{R}_3\text{NHCl})_4$ and $\text{UO}_2\text{Cl}_2(\text{R}_3\text{NHCl})_2$, in which R_3NHCl represents trilaurylamine chlorhydrate. The equilibria between the two phases are in the form:



The latter complex occurs only at high uranium concentrations in an aqueous solution. The partition coefficient depends on the amine concentration in cyclohexanol; at the amine concentration used (0.8 M), it depends only on the hydrochloric acid concentration in aqueous phase. By way of example, Fig. 10 shows the variations in the partition coefficients of iron (III), copper (II), uranium (VI), cesium (I) and strontium (II) as a function of HCl concentration. These curves show that although the partition coefficients are all fairly low, some separations may be predicted. Thus it is possible to separate uranium from copper, cesium and strontium, but not from iron (Fig. 11). /46

Extraction of Chelates

In this case the stationary phase is either a pure liquid chelating compound or a solution of an HA chelating compound in an organic solvent. The equilibrium between the two aqueous and organic phases is a true ion exchange equilibrium. The stationary phase is equivalent to a cation exchange resin in acid form, with the sole difference that the HA functional groups are not fixed on the carrier but are rather free in the stationary organic solution. The metallic cations are replaced by H^+ ions in the aqueous phase and their partition coefficient thus depends on the pH of the aqueous solution.

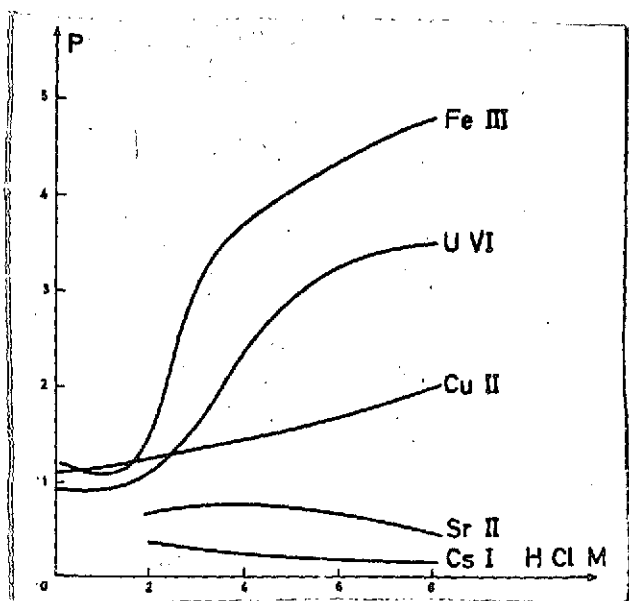


Fig. 10. Variations in partition coefficients of Fe III, U VI, Cu II, Sr II and Cs I between a 0.8 M solution of trilaurylamine in cyclohexanol fixed on porous Kel-F and aqueous hydrochloric acid solutions [4].

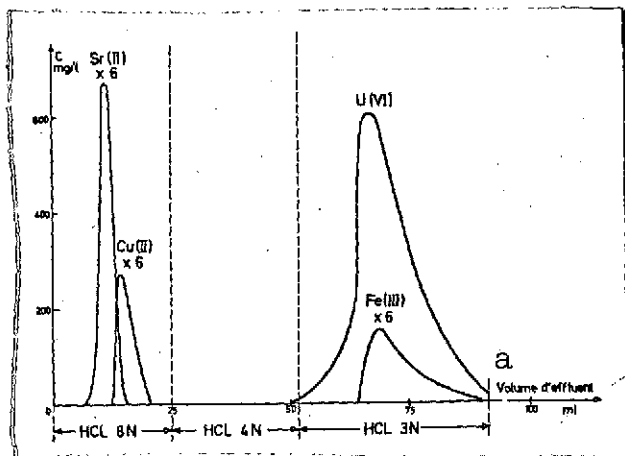
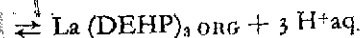
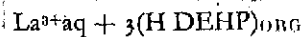


Fig. 11. Elution of a mixture of Cu (II), Sr(II), U(VI), and Fe(III) chlorides by means of a column of porous Kel-F saturated with a 0.8 M solution of trilaurylamine in cyclohexanol and aqueous hydrochloric acid solutions [4].

Key: a. Quantity of effluent in ml

For example, the extraction of lanthanum organophosphate by pure phosphoric diethylhexyl acid (H DEHP) fixed on porous Kel-F may be written:



Separation may be obtained by varying the pH of the eluant. Thus Cerrai and Testa [5] were able to separate the rare earths by graduated elution with the use of a hydrochloric acid solution of continuously variable concentration (Fig. 12).

Other Types of Extraction in the Organic Stationary Phase

A great deal of work has been done on chromatographic extraction in the organic stationary phase, and a number of applications, aside from the separations we have noted to illustrate this

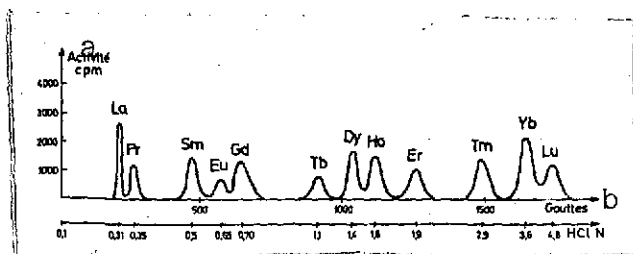


Fig. 12. Graduated elution of rare earths by hydrochloric acid on a column of porous Kel-F saturated with phosphoric diethyl-hexyl acid [5].

Key: a. Activity
b. Drops

[7], Testa [8] and Goret. [9].

The success of this method has been due primarily to the fact that the equilibria between the two phases are quickly obtained; in some cases it was possible to reach theoretical plate heights on the order of a millimeter. T

Conclusion

In any attempt to apply chromatography to a method of separation by extraction it may be seen that there is a choice of two possibilities:

- either the aqueous phase is fixed by means of an ion exchange resin;
- or the organic phase is fixed by means of an inert porous polymer.

These two techniques have their respective advantages and disadvantages.

If the aqueous phase is fixed, the elements to be separated/47 must be placed in an organic solution before they can be fixed on the column. This necessitates preliminary quantitative ex

principle, have been described in the literature over the last 10 years. Significant results have been obtained, especially by applying chromatographic techniques to extraction by tri-n-octylamine, tributylphosphate, and trioctylphosphine oxide. Detailed reports on these applications have been made by Markov [6], Carrai

extraction of the elements to be separated. In addition, there is a risk that the equilibria between the organic phase and the water-saturated resin will be slow. On the other hand, the main advantages of this method are as follows:

- the aqueous stationary phase is very firmly fixed to the support;
- the capacity of the column is high: this is the exchange capacity of the ion exchangers;
- preparation of the column is simple from a technical standpoint.

If the organic phase is fixed, there is a risk that certain problems involving the support will arise: the organic phase is not always very firmly fixed to the polymer; preparation of the columns is fairly problematic and the results of separation may heavily depend on this preparation; and the capacity of the column is 1/10 to 1/20 that of ion exchange resin columns. However, the main advantages of chromatography with a fixed organic phase are as follows:

- one works with an aqueous solution and recovers an aqueous solution;
- there is a fast rate of exchange between the two phases and the efficiency of the columns is satisfactory;
- it is possible to work at relatively high temperatures, given the heat resistance of inert polymers, which is superior to that of ion exchange resins.

It is therefore difficult to choose one method over another a priori. Systematic experimental analysis of the possibilities offered by each method would be useful. At any rate, there can be no doubt that development of these techniques will continue.

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